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Native donors and acceptors in molecular-beam epitaxial GaAs grown at 200 °C

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Absorption measurements at 1.1 and 1.2 μm were used along with the known electron and hole photoionization cross sections for EL2 to determine deep donor (EL2-like) and acceptor concentrations $N_D = 9.9 \times 10^{19}$ and $N_A = 7.9 \times 10^{18} \text{ cm}^{-3}$, respectively, in a 2- μm -thick molecular-beam epitaxial GaAs layer grown at 200 °C on a 2-in.-diam semi-insulating wafer. Both lateral and depth uniformities of N_D over the wafer were excellent as was also the case for the conductivity. Band conduction was negligible compared to hopping conduction at 296 K as evidenced by the lack of a measurable Hall coefficient.

Molecular-beam epitaxial (MBE) GaAs grown at low temperatures, 200–400 °C, has proven to be a uniquely interesting material and moreover has produced record-breaking performances in such devices as metal-insulator field-effect transistors and photoconductive switches.¹ It is generally agreed that its uniqueness lies in an abundance of native defects resulting from being As rich, including defects such as As antisites (As_{Ga}), As interstitials (As_i), As precipitates, and possibly Ga vacancies (V_{Ga}). Complexes of these defects as well as other independent defects could also exist, of course. However, quantification of the point defects, As_{Ga} , As_i , and V_{Ga} , has proven difficult for several reasons. First of all, only the As_{Ga} has an established fingerprint [by electron paramagnetic resonance (EPR) or optical absorption], and even then there is a problem because of the small thickness (2 μm) that can be grown in single crystal form at 200 °C, and because of the competition from the As_{Ga} (EL2) in the much thicker substrate. Also, the usual 1.1- μm absorption measures only the neutral fraction of the As_{Ga} , and EPR measures only the ionized fraction. (Usually, the ionized fraction is taken to be the same as the acceptor concentration N_A since free carriers are negligible in this type of material. This assumption will be true if shallower donors are negligible and if the EPR sees all of the possibly different As_{Ga} species.) The results of such measurements typically give $[\text{As}_{\text{Ga}}]^0 \approx 10^{19}$ – 10^{20} cm^{-3} and $[\text{As}_{\text{Ga}}]^+ \approx N_A \approx 1$ – $5 \times 10^{18} \text{ cm}^{-3}$. In this letter, we have carried out absorption measurements at two wavelengths, 1.1 and 1.2 μm , and then used the known electron and hole photoionization cross sections² to determine both $[\text{As}_{\text{Ga}}]^0$ and $[\text{As}_{\text{Ga}}]^+$. Thus, for the first time, we have deduced the total $[\text{As}_{\text{Ga}}]$ (since $[\text{As}_{\text{Ga}}] = [\text{As}_{\text{Ga}}]^0 + [\text{As}_{\text{Ga}}]^+$) and the acceptor concentration ($N_A \approx [\text{As}_{\text{Ga}}]^+$) in a small sample area (1/2 \times 1/2 mm), and we have mapped these quantities over a 2-in. wafer. The absorption due to the substrate was accounted for, as described below. Also, the depth uniformity of As_{Ga} as well

as that of the conductivity were measured on selected samples by etching experiments. A Hall coefficient could not be measured, suggesting that band conduction was negligible compared to hopping conduction.

In the absorption experiment, the fractional transmission T is measured, where

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}. \quad (1)$$

Here, R is the reflectance, α is the effective absorption coefficient, and d is the effective thickness. For the case of a GaAs layer of thickness d_l on a GaAs substrate of thickness d_s , it is easy to show that

$$\alpha d = \alpha_l d_l + \alpha_s d_s. \quad (2)$$

In the substrate it is known that most of the absorption over the wavelength range 0.9 to 1.8 μm is due to EL2 ($\sim \text{As}_{\text{Ga}}$) which has well-known electron and hole photoionization coefficients $\sigma_{n\lambda}$ and $\sigma_{p\lambda}$, respectively.² Since the shape of the absorption spectrum in 200 °C MBE GaAs is nearly equal to that in the substrate,³ and it is known that As_{Ga} is involved in both cases, it is assumed that the same $\sigma_{n\lambda}$ and $\sigma_{p\lambda}$ also hold in the layer. Then

$$\alpha_{l\lambda} = \sigma_{n\lambda} [\text{As}_{\text{Ga}}]_l^0 + \sigma_{p\lambda} [\text{As}_{\text{Ga}}]_l^+ \quad (3)$$

with a similar equation for $\alpha_{s\lambda}$. Since $[\text{As}_{\text{Ga}}]_s^0$ and $[\text{As}_{\text{Ga}}]_s^+ \approx N_A$ are known for the substrate, we can calculate $\alpha_s d_s$ and subtract that quantity from the measured αd to get $\alpha_l d_l$. By doing this at two wavelengths, it is possible to get both $[\text{As}_{\text{Ga}}]_l^0$ and $[\text{As}_{\text{Ga}}]_l^+$, or equivalently, the total $[\text{As}_{\text{Ga}}]$ and N_A . We have chosen $\lambda = 1.1$ and 1.2 μm , partly because at 1.2 μm , $\sigma_n \approx \sigma_p$ at 296 K, so that $\alpha_{1.2} = \sigma_{n1.2} [\text{As}_{\text{Ga}}]$. To totally remove the effects of the substrate as well as any residual absorption, and to determine $[\text{As}_{\text{Ga}}]$ and N_A as a function of depth, we can do differential absorption measurements while etching the layer in steps. For this experiment, it is straightforward to show that

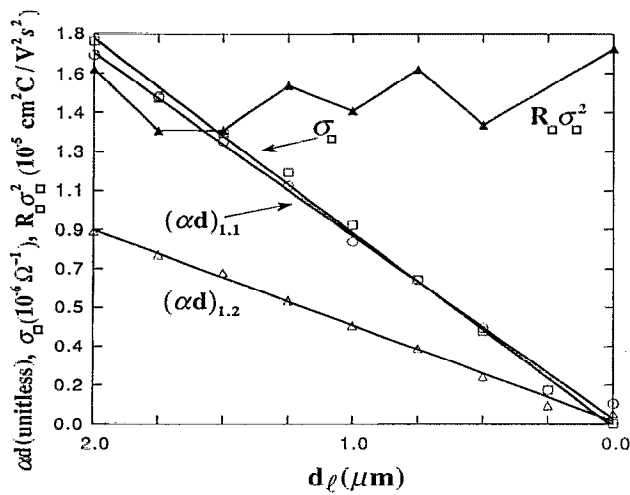


FIG. 1. The measured quantities αd , σ_{\square} , and $R_{\square}\sigma_{\square}^2$ as a function of layer thickness.

$$[\text{As}_{\text{Ga}}] = \frac{1}{\sigma_{n1.2}} \frac{d(\alpha d)_{1.2}}{d(d_{\ell})}, \quad (4)$$

$$[\text{As}_{\text{Ga}}]^+ = \frac{1}{(\sigma_{n1.1} - \sigma_{p1.1})} \left[\frac{\sigma_{n1.1}}{\sigma_{n1.2}} \frac{d(\alpha d)_{1.2}}{d(d_{\ell})} - \frac{d(\alpha d)_{1.1}}{d(d_{\ell})} \right]. \quad (5)$$

The cross sections given in the literature are $\sigma_{n1.1} = 9.07 \times 10^{-17}$, $\sigma_{p1.1} = 3.2 \times 10^{-17}$, $\sigma_{n1.2} = 4.8 \times 10^{-17}$, and $\sigma_{p1.2} = 4.72 \times 10^{-17} \text{ cm}^2$.^{2,4} However, to apply Eq. 4 we have used $\sigma_{n1.2} = \sigma_{p1.2} = 4.8 \times 10^{-17}$ with little additional error.

The results of the etching experiment are shown in Fig. 1. The sample was a non-In-bonded, 2- μm layer grown with As_4 directly on a semi-insulating substrate in a Varian GEN II MBE apparatus. The thermocouple temperature was set at 200 °C and a beam-equivalent pressure ratio $\text{As}_4/\text{Ga} = 20$ was used. The reflection high-energy electron diffraction pattern was consistent with single-crystal growth over the full 2 μm . Etching was accomplished with a 1:1:40 $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution which removed about 25 Å/s. As seen in Fig. 1, the slopes of the $(\alpha d)_{1.1}$ and $(\alpha d)_{1.2}$ lines are nearly constant over most of the layer, which suggests good uniformity as a function of depth. The values of $[\text{As}_{\text{Ga}}]$ and $[\text{As}_{\text{Ga}}]^+$ given by Eqs. (4) and (5) are $(9.9 \pm 0.5) \times 10^{19} \text{ cm}^{-3}$ and $(8 \pm 6) \times 10^{18} \text{ cm}^{-3}$. The large uncertainty in $[\text{As}_{\text{Ga}}]^+$ is calculated from an assumed uncertainty of only $\pm 5\%$ in the ratio $\sigma_{n1.1}/\sigma_{n1.2}$. Thus, it is clear that this ratio, as well as the slopes of $(\alpha d)_{1.1}$ and $(\alpha d)_{1.2}$ vs d_{ℓ} , will have to be known very accurately to get better results for N_A .

We also measured the Hall effect at each etch step. These measurements will be discussed in more detail elsewhere, but it can be shown that $d\sigma_{\square}/d(d_{\ell}) = \sigma_I$ and $d(R_{\square}\sigma_{\square}^2)/d(d_{\ell}) = R_{\square}\sigma_I^2$. From the slopes in Fig. 1, we can calculate $\sigma_I^{-1} = \rho_I = (1.13 \pm 0.05) \times 10^2 \Omega \text{ cm}$, uniform in depth over most of the layer, and $R_{\square}\sigma_I^2 \approx 0 \pm 5 \times 10^{-3} \text{ cm C/V}^2 \text{ s}^2$. The latter result suggests that the Hall coefficient in the layer (which must be due to band conduction since the stronger hopping conduction produces no Hall coefficient) is overwhelmed by the Hall coefficient in the

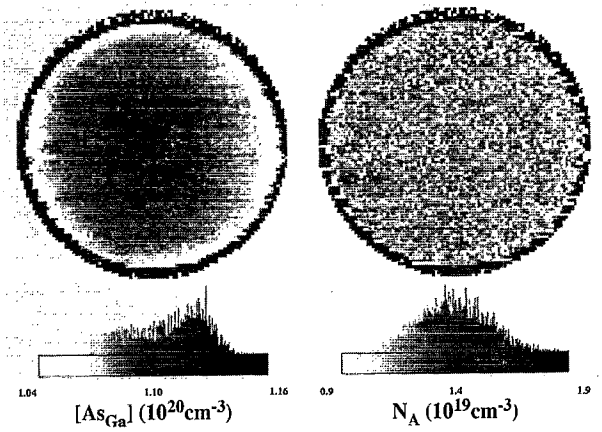


FIG. 2. Maps of $[\text{As}_{\text{Ga}}]$ and N_A for a 2- μm -thick MBE GaAs layer grown at 200 °C on a 2-in.-diam semi-insulating GaAs wafer.

substrate; i.e., $R_{\square}\sigma_{\square}^2 \approx R_{\square}\sigma_s^2 d_s$. Thus, the analysis presented in Ref. 5 to determine N_A [$\approx (\text{As}_{\text{Ga}})^+$] cannot be used, since N_A is determined from R_I in the Hall-effect method. However, N_D ($\approx [\text{As}_{\text{Ga}}]$) can still be calculated from that analysis, because N_D strongly affects the hopping conductivity, which dominates the conductivity in the layer. A preliminary temperature-dependent analysis of σ_I gives $[\text{As}_{\text{Ga}}] \approx 9.7 \times 10^{19} \text{ cm}^{-3}$, which is in good agreement with the $9.9 \times 10^{19} \text{ cm}^{-3}$ measured by absorption.

The lateral uniformity of $[\text{As}_{\text{Ga}}]$ and $[\text{As}_{\text{Ga}}]^+$ is presented in the gray scale maps of Fig. 2. Here, αd_{ℓ} at each point was corrected by subtracting from each measured αd an averaged value of $\alpha_s d_s$, where α_s was calculated by assuming $[\text{As}_{\text{Ga}}]_s \approx 1.0 \times 10^{16}$ and $[\text{As}_{\text{Ga}}]_s^+ \approx N_A \approx 1 \times 10^{15} \text{ cm}^{-3}$, which are representative values for these wafers. Of course, the numbers in Fig. 2 are not as accurate as those determined by the etching technique (Fig. 1), but still they are within our error estimates. The $[\text{As}_{\text{Ga}}]$ pattern on the left-hand side qualitatively reflects the expected variation in substrate temperature, i.e., hotter near the periphery because of the placement of the heater rings. In spite of this fact, the standard deviation across the whole wafer is only about 3% and only about 1% over the center-half of the wafer. Such good uniformity is necessary for integrated circuit applications. The lateral variation of N_A appears to be considerably higher, with a standard deviation of about 15%, but again it must be remembered that there is much more uncertainty in the calculation of N_A .

In summary, we have measured both the lateral and depth variations of $[\text{As}_{\text{Ga}}]$ and $[\text{As}_{\text{Ga}}]^+ \approx N_A$ on a 2- μm MBE layer grown at 200 °C on a 2-in. GaAs wafer. The average value of $[\text{As}_{\text{Ga}}]$ agrees well with that deduced from temperature-dependent conductivity measurements on the same sample, and the average value of N_A is consistent with EPR results reported in the literature.^{6,7} Variations of the $[\text{As}_{\text{Ga}}]$ across the wafer reflect the expected substrate temperature variation during growth but are still quite small, with a standard deviation of only about 3%.

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